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TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		Atty. Docket No. FRD-043  U.S. APPLICATION NO. (If known, see 37 CFR 1.5) <b>09/673121</b>
INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/NO99/00116 ✓	April 7, 1999 ✓	April 8, 1998 ✓
TITLE OF INVENTION		
Catalyst System for Ethylene Polymerisations ✓		
APPLICANT(S) FOR DO/EO/US		
Follestad et al. ✓		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
<p>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l).</p> <p>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19<sup>th</sup> month from the earliest claimed priority date.</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <ul style="list-style-type: none"> <li>a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ul> <p>6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(C)(3))</p> <ul style="list-style-type: none"> <li>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> have been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input type="checkbox"/> have not been made and will not be made.</li> </ul> <p>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).</p> <p>9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(C)(5)).</p>		
Items 11. to 16. below concern document(s) or information included:		
<p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment.</p> <p><input type="checkbox"/> A SECOND OR SUBSEQUENT preliminary amendment.</p> <p>14. <input type="checkbox"/> A substitute specification.</p> <p>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>16. <input checked="" type="checkbox"/> Other items or information:            Copy of PCT Notice Form PCT/IB/308            Copy of PCT Notice Form PCT/IB/332            Copy of PCT Notice Form PCT/IB/306            Inventor Data Sheet         </p>		

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17. <input checked="" type="checkbox"/> The following fees are submitted:				<u>CALCULATIONS</u>	PTO USE ONLY																								
<b>BASIC NATIONAL FEE (37 CFR 1.492 (a)(1) - (5)):</b>																													
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International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) .....																													
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				\$ 860.00																									
Surcharge of \$130.00 for furnishing the oath or declaration of later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$																									
<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th>CLAIMS</th> <th>NUMBER FILED</th> <th>NUMBER EXTRA</th> <th>RATE</th> <th colspan="2"></th> </tr> </thead> <tbody> <tr> <td>Total claims</td> <td>12 - 20 =</td> <td>0</td> <td>X \$18.00</td> <td>\$ 00.00</td> <td></td> </tr> <tr> <td>Independent claims</td> <td>2 - 3 =</td> <td>0</td> <td>X \$78.00</td> <td>\$ 00.00</td> <td></td> </tr> <tr> <td>MULTIPLE DEPENDENT CLAIM(S) (if applicable)</td> <td></td> <td></td> <td>+ \$260.00</td> <td>\$</td> <td></td> </tr> </tbody> </table>						CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE			Total claims	12 - 20 =	0	X \$18.00	\$ 00.00		Independent claims	2 - 3 =	0	X \$78.00	\$ 00.00		MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$260.00	\$	
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Reduction of ½ for filing by small entity, if applicable. A Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28)				\$																									
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Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				\$																									
<b>TOTAL NATIONAL FEE =</b>				\$ 860.00																									
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$																									
<b>TOTAL FEES ENCLOSED =</b>				\$ 840.00																									
				<b>Amount to be:</b>	\$																								
				<b>refunded</b>																									
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- a.  A check in the amount of \$840.00 to cover the above fees is enclosed.
- b.  Please charge my Deposit Account No. 20-0531 in the amount of \$20.00 only to cover the shortfall in the check for the above fees.
- c.  The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 20-0531.

NOTE: When an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Patent Administrator  
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125 High Street  
High Street Tower  
Boston, MA 02110

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SIGNATURE

Christopher W. Stamos  
NAME

35,370  
REGISTRATION NUMBER

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## IN THE UNITED STATES ELECTED OFFICE (EO/US)

International Application No.: PCT/NO99/00116

International Filing Date: April 7, 1999

Title: Catalyst System For Ethylene Polymerisations

Attorney's Docket No.: FRD-043

Box PCT, Attention: EO/US  
Commissioner of Patents and Trademarks  
Washington, D. C. 20231

PRELIMINARY AMENDMENT

Please amend the application as follows, without prejudice.

IN THE CLAIMS

Please amend claims 1-12.

1. (amended) A catalyst system for [the] polymerisation of ethylene, comprising chromium oxide and a metallocene supported on an inorganic support, characterised by:

- a) said support being a particulate inorganic oxide;
- b) [the] chromium of said chromium oxide being in a reduced oxidation state,

and

- c) a metallocene compound having [the] a formula:



wherein each Cp, being equal or different, is an unsubstituted or substituted cyclopentadienyl compound, and R' and R'', independant of each other, are selected from the group [comprising] consisting of alkyls having 1 to 6 carbon atoms, unsubstituted or substituted benzyl, and phenoxy substituted with alkyls having 1 to 6 carbon atoms, and R' or R'' may be a halide.

2. (amended) A catalyst system according to claim 1, characterised in that the cyclopentadienyl compound is substituted with radicals selected from the group [comprising]

consisting of unsubstituted and substituted linear, branched, cyclic or partially cyclic alkyl radicals and annelated cyclic radicals, containing 1 to 20 carbon atoms; unsubstituted and substituted monocyclic or polycyclic aryl radicals which optionally also may contain hetero atoms; and aralkyl radicals; [the] wherein substituents on the cyclopentadienyl ring may also form annelated structures comprising one or more fused benzene, naphtalene or cyclohexene rings, which optionally may contain hetero atoms, and the two cyclopentadienyl rings may also be connected through a bridge.

3. (amended) A catalyst system according to claim 1, characterised in that R' and R" are selected from the group [comprising] consisting of chloride, methyl, benzyl or phenoxyethyl, and combinations thereof.
4. (amended) A catalyst system according to claim[s] 1 [to 3], characterised in that Cp is an unsubstituted cyclopentadienyl and that R' and R" are equal and are either methyl or benzyl.
5. (amended) A catalyst system according to claim[s] 1 [to 4], characterised in that the metallocene is bis-cyclopentadienylzirconium dibenzyl.
6. (amended) A catalyst system according to claim 1, characterised in that said support is a particulate, inorganic oxide selected from the group [comprising] consisting of alumina, silica, titania, zirconia, magnesia, and combinations thereof.
7. (amended) A catalyst system according to claim 6, characterised in that said support is silica having [the] a shape of spherical or spheroidal particles with a particle size in [the] a range of from 20 µm to 150 µm, and a surface area from 200 m<sup>2</sup>/g to 600 m<sup>2</sup>/g.
8. (amended) A catalyst system according to claim 1, characterised in that the chromium is present in an amount from 0.1 % to 10 % by weight calculated as metallic chromium based on [the] weight of the chromium/silica catalyst of a) and b).

9. (amended) A catalyst system according to claim 8, characterised in that the chromium is present in an amount from 0.5 to [2,0] 2.0 % by weight of chromium.

10. (amended) A catalyst system according to claim 1 [to 5], characterised by a molar ratio between zirconium and chromium in the final catalyst in [the] a range from 0.1:1 to not higher than 2:1.

11. (amended) A catalyst system according to claim [9] 10, characterised in that said molar ratio between zirconium and chromium is from 0.5:1 to 1:1.

12. (amended) A method for the preparation of [the] a catalyst system for polymerisation of ethylene, comprising chromium oxide and a metallocene supported on an inorganic support [of claim 1], the method comprising the steps of:

- a) calcining a support being a particulate, inorganic oxide selected from the group [comprising] consisting of alumina, silica, titania, zirconia, magnesia, and combinations thereof,
- b) joining onto [the] a surface of said support a chromiumorganic compound to obtain a catalyst precursor,
- c) subjecting said catalyst precursor to oxidising conditions to obtain [the] chromium in an oxidised state, and
- d) subjecting said catalyst precursor to reducing conditions to obtain a prereduced catalyst, characterised by
- e) reducing the oxidised chromium to obtain [the] a main part thereof in a bivalent oxidation state, and
- f) contacting said reduced catalyst with a metallocene compound having [the] a formula:



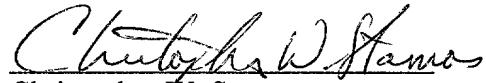
wherein each Cp, equal or different, is an unsubstituted or substituted cyclopentadienyl compound, and R' and R'', independant of each other, are selected from the group [comprising] consisting of alkyls having 1 to 6 carbon atoms, unsubstituted or substituted benzyl, and phenoxy substituted with alkyls having 1 to 6 carbon atoms, and R' or R'' may be a halide.

REMARKS

This Preliminary Amendment is being submitted to correct typographical errors in the claims, convert a number of multiple dependent claims to dependent claims, and to conform the claims to U.S. patent practice. No new matter is being introduced thereby.

Applicants respectfully request entry of this amendment prior to examination of the application on the merits.

Respectfully submitted,

  
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Date: October 10, 2000

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09/673121CATALYST SYSTEM FOR ETHYLENE POLYMERISATIONS

## TECHNICAL FIELD

The present invention relates to a supported chromium oxide catalyst, in particular a catalyst system comprising an inorganic support, a chromium oxide and a metallocene compound, and a method for the preparation of said catalyst system. The catalyst produces branched polyethylenes without the use of a copolymer, and the molecular weight can be controlled by feeding hydrogen.

10

## BACKGROUND ART

To obtain linear polyolefins having desired properties, different catalyst systems in combinations with controlled polymerisation conditions are used. A typical supported chromium catalyst that is extensively used in commercial polymerisations of ethylene is formed by depositing a chromium compound onto a support, which is then oxidised. The oxidised catalyst precursor may be introduced as such into a polymerisation reactor, where it will be reduced in situ by the olefin monomers to its active catalytic state. It is also well known that oxidised chromium compounds may be prereduced by suitable reagents, such as hydrogen or carbon-monoxide (J.P. Hogan, J. Polym. Sci., PtA-1, 8, 2637 (1970), and references therein). The resulting chromium surface species are generally accepted to be highly reactive. A prereduced chromium-based catalyst will produce polyethylenes having a broad molecular weight distribution (MWD) and mainly long, straight chains. Such catalysts are not hydrogen-sensitive.

Another commercially important class of catalysts used to polymerise  $\alpha$ -olefins are the cyclopentadienyl transition metal catalysts, usually termed metallocene catalysts. Metallocenes contacted with Lewis acids will give effective polymerisation catalysts that produce linear polyethylenes having a narrow molecular weight distribution (MWD). Such catalysts are sensitive to the presence of hydrogen.

By adding comonomers and optionally hydrogen during the catalysed polymerisation reactions the density and chain branching of the produced polymer can be controlled. In the prior art efforts have

been made to develop combined catalyst systems that produce short chain branched polyethylenes, without the addition of comonomers during the polymerisation reactions.

5 US Patent 4,735,931 discloses a catalyst system prepared by first depositing a chromium compound on a predominantly silica support, activating said catalyst in an oxygen-containing atmosphere and thereafter subjecting the thus activated composition to reduction with carbon monoxide. The resulting  
10 chromium catalyst composition is then precontacted with a cocatalyst selected from trialkyl boron and dialkyl aluminium alkoxide compounds, preferably triethyl borane, and thereafter contacted with ethylene. When used in olefin polymerisations this catalyst provides in situ generation of comonomers, resulting in  
15 tough, flexible, mainly pure polyethylene resins.

US Patent 5,032,651 teaches the use of catalyst mixtures of two transition metal catalysts. One of the catalysts comprises chromium oxide supported on an aluminophosphate, and the other  
20 one comprises a  $\beta$ -stabilized tetrahydrocarbyl zirconium compound supported on an inorganic material. The catalysts may be premixed before use, or they may be fed separately to the reactor. Olefinic polymers exhibiting high environmental stress crack resistance (ESCR) are produced.

25 EP 206794 describes an olefin polymerisation catalyst comprising a support contacted with a Group 4b, 5b or 6b metallocene and an aluminoxane.

30 EP 088 562 discloses a modified polymerisation catalyst comprising a silica support with deposited chromium. Following oxidation in dry air, the chromium is modified by being contacted with a transition metal compound of Ti, V or Cr, preferably Ti. Only the use of bis-toluene titanium is exemplified, and the  
35 obtained polyethylenes have a substantial degree of branching and a medium or broad molecular weight distribution.

US 3,378,536 discloses a process for the polymerisation of ethylene by the use of a two-component catalyst system consisting

of (a) a chromium compound deposited on e.g. silica, where the chromium being activated in an oxygen-containing gas at a high temperature and then reduced with CO; and (b) chromium or vanadium arene where the arene is an aromatic, optionally substituted C<sub>6</sub> ring. The two catalyst components are preferably fed separately to the polymerisation reactor.

It is well known to a person skilled in the art that the various processing techniques used in the manufacturing of final articles from polyethylene resins require polyethylene grades having specific rheological properties. For instance, in the extrusion blow moulding of containers polyethylenes having a broad MWD and long straight chains are typically used, while in film blowing lower density polyethylenes are preferred.

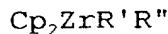
It is an object of the present invention to provide a novel catalyst system that produces a branched polyethylene from ethylene without any addition of comonomer during the polymerisation reaction. A further object is to control the polymerisation reaction to produce polyethylenes having a desired density and molecular weight. Another object is to obtain polyethylene resins suitable for use blow moulding and film blowing processing.

It has now been found that a catalyst system comprising a prereduced chromium on silica catalyst that have been contacted with a metallocene compound fulfils the requirements above. The novel catalyst system produces a branched low density polyethylene polymer without any added comonomer. The density and molecular weight (and hence the melt flow index) of the polymer can be controlled by the addition of hydrogen to the reactor.

#### DISCLOSURE OF INVENTION

The present invention thus provides a catalyst system for the polymerisation of ethylene, comprising chromium oxide supported on an inorganic support, wherein

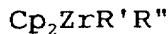
- said support being a particulate inorganic oxide;
- the chromium of said chromium oxide being in a reduced oxidation state, and comprising
- a metallocene compound having the formula:



wherein each Cp, being equal or different, is an unsubstituted or substituted cyclopentadienyl compound, and R' and R'', independant of each other, are selected from the group comprising alkyls having 1 to 6 carbon atoms, unsubstituted or substituted benzyl, and phenoxy substituted with alkyls having 1 to 6 carbon atoms, and R' or R'' may be a halide.

The invention also provides a method for the preparation of the catalyst system above, comprising the steps of:

- a) calcining a support being a particulate, inorganic oxide selected from the group comprising alumina, silica, titania, zirconia, magnesia, and combinations thereof,
- b) joining onto the surface of said support a chromium-organic compound to obtain a catalyst precursor,
- c) subjecting said catalyst precursor to oxidising conditions to obtain the chromium in an oxidised state,
- d) subjecting said catalyst precursor to reducing conditions to obtain a prereduced catalyst, thus
- e) reducing the oxidised chromium to obtain the main part thereof in a bivalent oxidation state,
- f) contacting said reduced catalyst with a metallocene compound having the formula:



wherein each Cp, equal or different, is an unsubstituted or substituted cyclopentadienyl compound, and R' and R'', independant of each other, are selected from the group comprising alkyls having 1 to 6 carbon atoms, unsubstituted or substituted benzyl, and phenoxy substituted with alkyls having 1 to 6 carbon atoms, and R' or R'' may be a halide.

#### BEST MODES FOR CARRYING OUT THE INVENTION

The catalyst system of the present invention comprises a supported reduced chromium/silica catalyst contacted with a metallocene compound. In general, metallocenes based on zirconium, hafnium and titanium are preferred as metallocene catalysts. By metallocenes are meant compounds in which a metal atom or ion or complex ion is  $\pi$ -bonded by at least one ligand, e.g. by 1, 2 or 3 ligands or ligand components. The  $\pi$ -bonding

ligands in such catalysts may be simple unsubstituted cyclopentadienyl rings, but preferably they will be optionally substituted fused ring systems (e.g. indenyl ligands), substituted cyclopentadienyl rings, optionally substituted bridged bis-cyclopentadienyl ligands or optionally substituted bridged bis fused ring systems (e.g. bis indenyl ligands).

- The catalyst support may be any oxide of metals from groups 2, 3, 4, 11, 12, 13 and 14 of the Periodic System of Elements.
- 10 Preferred metal oxides are magnesia, alumina, titania, zirconia and silica. A particularly preferred catalyst support is silica. Such a silica support must contain not less than 90% pure silica, with the remaining part may consisting of other oxides, such as oxides of aluminium, zirconium, titanium, magnesium and phosphor.
- 15 The support should consist of particles having preferably a spherical or spheroidal shape and a size from about 10 µm to 150 µm, more preferably from 20 µm to 120 µm, and a particle size distribution from narrow to broad within said ranges.
- 20 The chromium compound to be impregnated onto the silica support may be an inorganic chromium compound, such as chromium nitrate and chromium oxide, or an organic chromium compound, such as chromium acetate. Other chromium compounds are also useable. The chromium compound can be joined with the support in any way known
- 25 in the art, such as by coprecipitation with the silica support or addition to a silica gel after its formation, or after that it has been dried. A typical procedure of impregnation comprises the use of a water-soluble compound, or the use of an organo-chromium compound in an anhydrous hydrocarbon solution. The only
- 30 precondition is that the chromium compound can be oxidized to a chromium oxide. The amount of chromium compound joined with the inorganic support must be sufficient to obtain from 0.1% to 10%, preferably from 0.5% to 2.0%, by weight of chromium, calculated as metallic chromium based on the weight of the supported
- 35 chromium catalyst. When the impregnation is finished any possible remaining solvent is removed to obtain a dry solid.

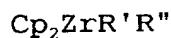
Such solid chromium oxide/silica catalyst precursors are also commercially available from a number of producers. A closer

description of their preparation is therefore regarded as being superfluous.

The obtained catalyst precursor must be activated before use.  
5 This is done by calcination in dry air or another oxygen-containing gas at temperatures in the range from 400 to 950 °C, preferably from 550 to 800 °C, during a period from 10 minutes to 24 hours, preferably from 2 to 20 hours. The oxidised catalyst precursor is conventionally subjected to reduction, preferably  
10 with carbon monoxide or a mixture of carbon monoxide and an inert component, such as nitrogen or argon. The reduction is normally performed at a temperature within the range from 300 to 500 °C, preferably from 350 °C to 400 °C, during a period from 5 minutes to 48 hours, preferably from 1 to 10 hours. When the reduction  
15 is completed, the major part of the contained chromium should preferably be in a bivalent oxidation state. The final chromium catalyst particles should have a surface area from 200 to 600 m<sup>2</sup>/g, more preferably from 300 to 550 m<sup>2</sup>/g, and a pore volume from 1 to 3 cm<sup>3</sup>/g. The chromium oxide/silica catalyst in a  
20 reduced state, either as a dry powder or as a slurry in a dry oxygen-free hydrocarbon solvent, e.g. an alkane, must be stored in an inert ambience.

The present invention is not restricted to any particular  
25 procedure for the preparation of the chromium oxide/silica catalyst, and other methods than those described here may also be applicable.

The obtained chromium oxide/silica catalyst is contacted with a  
30 cyclopentadienyl-zirconium compound, hereinafter termed "zirconocene". Preferred zirconocenes can be represented by the simplified formula:



wherein Cp designates cyclopentadienyl groups selected from  
35 unsubstituted cyclopentadienyl; cyclopentadienyl substituted with radicals selected from the group comprising unsubstituted and substituted linear, branched, cyclic or partially cyclic alkyl radicals, and annelated cyclic radicals, containing 1 to 20 carbon atoms; unsubstituted and substituted monocyclic or

polycyclic aryl radicals which optionally also may contain hetero atoms; and aralkyl radicals. The substituents on the cyclopentadienyl ring may also form annelated structures comprising one or more fused benzene, naphtalene or cyclohexene rings, which 5 optionally may contain hetero atoms. The substituents R' and R", equal or different, are selected from the group comprising alkyls having 1 to 6 carbon atoms, unsubstituted or substituted benzyl, and phenoxy substituted with alkyls having 1 to 6 carbon atoms. Preferably, R' and R" are independently selected from the group 10 comprising methyl, benzyl or fenoxyethyl, and any combination thereof. One or R' and R" may also be a halide, preferably chloride.

A number of suitable metallocene compounds of the formula above 15 are known in the art and have been recited in the literature. Particularly preferred metallocene compounds are embodied in the working examples.

Particularly good results are obtained when Cp represents cyclopentadienyl, and R' and R" are the same and are benzyl or methyl. 20

The zirconocene compound is joined with the activated prereduced chromium oxide/silica catalyst most conveniently by dissolving the zirconocene in a solvent, e.g. toluene, and impregnate the 25 chromium oxide/silica catalyst with this toluene solution. Eventually, the solvent is removed by evaporation, preferably in an inert atmosphere, whereupon the catalyst is ready for use.

The final catalyst will contain both zirconium and chromium, preferably in a molar ratio of zirconium to chromium in the range 30 from 0.1:1 to not higher than 2:1. More preferably the catalyst contains zirconium and chromium in a molar ratio from 0.5:1 to 1:1.

35 Prior to polymerisation, the catalyst may optionally be prepolymerised with a minor amount of ethylene and/or an  $\alpha$ -olefin in accordance with methods well known in the art, before being fed continuously to the polymerisation reactor.

DOCUMENTA PEGASUS

Polymerisations can be performed in any conventional type of reactor, such as in a batch reactor or most preferably in a continuous reactor. The present catalysts are suitable for use in all types of olefin polymerisations, including gas phase and suspension polymerisations. In general, polymerisations are performed at temperatures below 110 °C, and at a total pressure in the range from ambient to 50 bar. Hydrogen is used to control the molecular weight, and consequently the melt flow index, of the polymer, whereas the catalyst determines the short chain branching on the polyethylene backbone and hence the density of the polyethylene.

The general polymerisation parameters mentioned above are well known in the art and further details concerning ethylene polymerisations should be superfluous. Typical polymerisation conditions are presented in the examples below.

It is realized that the present catalyst system has its highest catalytic activity when the substituents R' and R" of the zirconocene compound are pure hydrocarbyl radicals, in the examples embodied as benzyl or methyl. A person skilled in the art will understand that similar hydrocarbyl compounds are expected to have the same effect and that such compounds are contemplated by the present invention. The catalysts of this invention provide substantially higher activities than the prior art chromium/-silica catalysts. When the substituents R' and R" contain hetero atoms, such as O and Cl, the present catalysts will get a reduced activity, typically lower than the activity of a comparative prior art chromium/silica catalyst. Thus, the activities of the catalysts of the present invention will be at their highest when the metallocene component is a pure hydrocarbyl zirconocene.

The present catalysts will have an activity that varies with the molar ratio between zirconium and chromium in the final catalyst. When the contained amount of zirconium is higher than the amount of chromium, the catalyst will have a lower catalytic activity than a comparative prior art chromium/silica catalyst. The present catalysts have their highest activity when the molar ratio between zirconium and chromium is about 0.5:1. This indi-

cates that only a minor amount of zirconocene is required to increase substantially the activity of a chromium/silica catalyst.

The catalytic activities of the present catalysts are also influenced by the concentration of hydrogen present in the polymerisation reactor. It has been found that an optimum level is about 1 bar of hydrogen.

The hydrogen level will also influence on the short chain branching of the produced polyethylenes. Analysis of polyethylenes polymerised with the present catalysts show that the obtained polymers have a higher amount of short chain branching than polyethylenes produced with a prior art chromium/silica catalyst. In particular, the amount of ethyl branches will increase. A higher level of hydrogen will increase the amount of short chain branching, in particular when using a catalyst having a ratio Zr/Cr of 0.5. By adjusting this ratio, as well as the hydrogen level inside the reactor, the morphology of the final resin can be controlled. Compared with the common used prior art chromium/silica catalysts, the catalysts of the present invention have a higher activity and will give a higher amount of short chain branching.

The present catalysts are preferably used to homopolymerise ethylene. However, it is also possible to use the present catalysts in copolymerisations of ethylene with a comonomer or a mixture of comonomers. Useful comonomers are all polymerisable  $\alpha$ -olefins having the general formula  $\text{CH}_2=\text{CHR}$ , wherein R is a hydrocarbon radical containing 1-18 carbon atoms, preferably 1-10 carbon atoms. Examples of particularly preferred  $\alpha$ -olefins are propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene. However, the greatest achievements of the present catalysts are in homopolymerisations of ethylene.

The produced polyethylenes will have a density from 910 to >960 kg/m<sup>3</sup>, and a melt index from 0.01 to above 100 g/10 min, preferably from 0.1 to 60 g/10 min (determined according to the method of ASTM 1238), depending on the polymerisation conditions, as explained above. More detailed specifications concerning the pro-

perties of the obtained polyethylenes are given in the examples.

## EXAMPLES

### Preparation of a Cr/SiO<sub>2</sub> catalyst

- 5 A catalyst support of silica having a surface area of 300 m<sup>2</sup>/g and a pore volume of 1.6 cm<sup>3</sup>/g was impregnated with an aqueous solution of CrO<sub>3</sub> in an amount sufficient to finally obtain 1 % by weight of Cr, calculated as metal based on the weight of the support. The impregnated support was reduced at 380 °C in a gas  
10 consisting of 5% of CO in nitrogen for 4 h, and then allowed to cool to ambient temperature in an inert atmosphere. For further use, the obtained blue-coloured catalyst was suspended in a dry, oxygen-free, purified mineral oil to a level of about 10 % by weight of catalyst.

15

### Synthesis of bis-cyclopentadienyl-zirconiumbenzyl (Cp<sub>2</sub>ZrBz<sub>2</sub>).

This zirconocene was prepared according to the method described by Fachinetti et al. in J. Chem. Soc., Chem. Commun., 1972, p. 654, by reacting 3 g of Cp<sub>2</sub>ZrCl<sub>2</sub> with 20.6 ml of a 1.0 M solution  
20 of BzMgCl (Bz=benzyl) in toluene at 0 °C for 1.5 h. The obtained yellow product was recrystallized from a mixture of toluene/heptane at -25 °C. The crystallized solid was collected by filtration and dried in vacuum.

### 25 Synthesis of bis-cyclopentadienyl-zirconiummethyl (Cp<sub>2</sub>ZrMe<sub>2</sub>)

This zirconocene was synthesized according to the method described by Wailes et al. in J. Organomet. Chem., Vol. 34, 1972, p. 155, by reacting 5 g of Cp<sub>2</sub>ZrCl<sub>2</sub> with 21.6 ml of MeLi (Me=methyl) in diethylether at 0 °C for 1 h. The precipitated  
30 LiCl was removed by filtration and the diethylether evaporated in vacuum to obtain a solid residue. This residue was heated at 80 °C and reduced pressure (2 to 10 torr). The obtained sublimed white crystalline Cp<sub>2</sub>ZrMe<sub>2</sub> was collected.

### 35 Synthesis of bis-cyclopentadienyl-zirconiummethyl(fenoxyethyl) (Cp<sub>2</sub>ZrMe(OPhMe))

To 4.84 ml of a 10% toluene solution of Cp<sub>2</sub>ZrMe<sub>2</sub> was added a stoichiometric amount of a 2.1% toluene solution of cresol at ambient temperature and allowed to react for 1 h. Methane was

released during the reaction.

**Synthesis of bis-cyclopentadienyl-zirconiummethylchloride ( $Cp_2ZrMe(Cl)$ )**

- 5 To 10 g of a 5% solution of  $Cp_2ZrMe_2$  was added slowly 48.7 ml gaseous HCl at 0 °C. The mixture was then allowed to reach ambient temperature and it was kept at this temperature overnight to complete the reaction.

10 **General procedure for the preparation of zirconocene-containing catalysts**

A synthesized zirconocene compound was contacted with the Cr/SiO<sub>2</sub> catalyst above. In an inert atmosphere at ambient temperature the zirconocene was added dropwise to a 10 % slurry of the Cr/SiO<sub>2</sub> catalyst and the reaction mixture stirred for at least 1 h to complete the reaction.

**General polymerisation procedure**

A 1 l laboratory stainless steel batch reactor equipped with a 20 paddle stirrer was heated to a desired temperature between 90 °C and 100 °C and purged with nitrogen, then 1.5 ml of the catalyst slurry was introduced and a desired amount of hydrogen was fed to the reactor. Then 0.5 l of i-butane was added to act as a diluent, whereupon ethylene was introduced until a total pressure 25 of 31.0 bar. The overall pressure was kept constant during the entire polymerisation run by feeding ethylene. The reactor temperature was kept constant at the fixed temperature to an accuracy of ±0.5 °C by automatically adjusting the heating and/or cooling of the reactor. Polymerisation times were from 20 and 40 30 minutes.

**EXAMPLES 1 TO 8**

These examples demonstrate the polymerisation of ethylene in the presence of a catalyst containing one of the various zirconocene 35 compounds synthesised above. The examples show that the catalysts comprising Cr/SiO<sub>2</sub> contacted with  $Cp_2ZrBz_2$  or  $Cp_2ZrMe_2$ , have the highest polymerisation activities. In all examples the molar ratio Zr/Cr equalled 1, the polymerisation temperature was in the range from 93 °C to 98 °C, and the H<sub>2</sub> pressure was either 1.0 or

0.5 bar. Polymerisation parameters and obtained results are given in table 1.

#### EXAMPLES 1 AND 2

5 Polymerisation catalyst: Cr/SiO<sub>2</sub> contacted with Cp<sub>2</sub>ZrBz<sub>2</sub>. In a 20 ml vial 0.510 g of the prepared Cr/SiO<sub>2</sub> catalyst (containing 1% Cr) was suspended in 4.168 g of mineral oil and the bottle closed with a septum. By the use of a syringe 0.375 ml of a 10% toluene solution of Cp<sub>2</sub>ZrBz<sub>2</sub> was added while stirring 10 by the use of a magnet bar, and the stirring continued for 1 h more. The obtained catalyst was used in the polymerisation of ethylene according to the general polymerisation procedure described above.

15 EXAMPLES 3 AND 4

Polymerisation catalyst: Cr/SiO<sub>2</sub> contacted with Cp<sub>2</sub>ZrMe<sub>2</sub>.

The procedure of Examples 1 and 2 was followed, except that the catalyst was prepared by adding 0.251 ml of a 10% solution of Cp<sub>2</sub>ZrMe<sub>2</sub>.

20

#### EXAMPLES 5 AND 6

Polymerisation catalyst: Cr/SiO<sub>2</sub> contacted with Cp<sub>2</sub>ZrMe(OPhMe).

The procedure of examples 1 and 2 was followed, except that the catalyst was prepared by adding 0.342 ml of a 10% solution of 25 Cp<sub>2</sub>ZrMe(OPhMe).

#### EXAMPLES 7 AND 8

Polymerisation catalyst: Cr/SiO<sub>2</sub> contacted with Cp<sub>2</sub>ZrMe(Cl).

The procedure of examples 1 and 2 was followed, except that the 30 catalyst was prepared by adding 0.342 ml of a 5 % solution of Cp<sub>2</sub>ZrMe(OPhMe).

#### EXAMPLE 9 (COMPARATIVE EXAMPLE)

Polymerisation catalyst: Cr/SiO<sub>2</sub>.

35 The procedure of examples 1 and 2 was followed, except that the catalyst was prepared by suspending 2 g of the Cr/SiO<sub>2</sub> prepared above in 16.691 g of mineral oil in a 50 ml glass bottle which was sealed with a septum. An amount of 1.5 ml of the catalyst slurry was withdrawn and used in a polymerisation run.

The results presented in Table 1 show that the pure hydrocarbyl zirconocenes of Examples 1 and 2,  $\text{Cp}_2\text{ZrBz}_2$ , and 3 and 4,  $\text{Cp}_2\text{ZrMe}_2$ , gave increased polymerisation activities compared with the standard prior art Cr/Si catalyst. On the other hand, the catalysts of Examples 5 and 6 containing hydrocarboxy substituents, and of Examples 7 and 8 containing chloride substituents, have lower activities than the prior art catalyst of Example 9. Further, the results show that the catalytic activity of the catalyst of Examples 1 and 2 depends on the hydrogen level present during polymerisation, and also properties like MFR and density of the produced polyethylene vary with the hydrogen concentration. Thus, the properties of the produced polyethylene can be controlled by regulating the hydrogen feed to the polymerisation reactor. The catalyst of Examples 3 and 4 shows the same tendency, but less pronounced. The activities of the catalysts of Examples 5 and 6, and 7 and 8, show a much less response to the presence of hydrogen.

TABLE 1  
Polymerisation of ethylene in the presence of catalyst Cr/silica + Cp<sub>2</sub>ZrR' R"

Ex.	R'	R"	Zr/Cr	H <sub>2</sub> (bar)	Temp. (°C)	Activity g/g·h	MFR g/10 min	Density g/cm <sup>3</sup>
Ex. 1	Bz	Bz	1	0.5	93	1054	0.09	0.933
Ex. 2	Bz	Bz	1	1.0	98	788	0.35	0.945
Ex. 3	Me	Me	1	0.5	93	1005	0.006	0.946
Ex. 4	Me	Me	1	1.0	94	849	0.017	0.947
Ex. 5	Me	OPhMe	1	0.5	93	338	0.004	0.952
Ex. 6	Me	OPhMe	1	1.0	97	341	0.03	0.952
Ex. 7	Me	C1	1	0.5	93	383	0.01	0.950
Ex. 8	Me	C1	1	1.0	97	392	0.05	0.047
Comp. 9	-	-	-	1.0	97	617	0.09	0.949

## EXAMPLES 10 TO 16

These examples demonstrate the relation between catalytic activity and the ratio Zr/Cr of the catalyst in the polymerisations of ethylene. The catalyst of Examples 1 and 2,  $\text{Cp}_2\text{ZrBz}_2$ , and of Examples 3 and 4,  $\text{Cp}_2\text{ZrMe}_2$ , were used. The general polymerisation procedure above was followed.

## EXAMPLE 10

Polymerisation catalyst: Cr/SiO<sub>2</sub> contacted with  $\text{Cp}_2\text{ZrBz}_2$ , having a Zr/Cr molar ratio of 0.25:1.

The catalyst was prepared analogous to example 1 by suspending 1.750 g of prereduced 1% by weight Cr/SiO<sub>2</sub> in 14.685 g of mineral oil in a 50 ml glass bottle provided with a septum. To this mixture was added 0.352 ml of 10% by weight  $\text{Cp}_2\text{ZrBz}_2$  in toluene, and the mixture was stirred for another 1 h. The obtained catalyst was then used in the polymerisation of ethylene.

## EXAMPLE 11

The polymerisation catalyst was prepared as in Example 10, except that 0.5 g of Cr/SiO<sub>2</sub> was suspended in 4.801 g of mineral oil in a 20 ml glass bottle, and 0.201 ml of a 10% by weight solution of  $\text{Cp}_2\text{ZrBz}_2$  in toluene was added to obtain a Zr/Cr ratio of 0.5:1.

## EXAMPLE 12

The catalyst was prepared as in Example 11, except that 0.403 ml of a 10% by weight solution of  $\text{Cp}_2\text{ZrBz}_2$  in toluene was added to obtain a Zr/Cr molar ratio of 1:1.

## EXAMPLE 13

The catalyst was prepared as in Example 11, except that 0.806 ml of a 10% by weight solution of  $\text{Cp}_2\text{ZrBz}_2$  in toluene was added to obtain a Zr/Cr molar ratio of 2:1.

## EXAMPLE 14

Polymerisation catalyst: Cr/SiO<sub>2</sub> contacted with  $\text{Cp}_2\text{ZrMe}_2$ , having a Zr/Cr molar ratio of 0.5:1.

The catalyst was prepared analogous to example 3 by suspending 1 g of Cr/SiO<sub>2</sub> in 8.327 g of mineral oil in a 50 ml glass bottle

16

provided with a septum. To this mixture was added 0.251 ml of a 10% by weight solution of  $\text{Cp}_2\text{ZrMe}_2$  in toluene, and the mixture was stirred for another 1 h.

5 EXAMPLES 15 AND 16

The catalyst was prepared as in Example 14, except using 0.502 ml and 1.004 ml of the 10% by weight solution of  $\text{Cp}_2\text{ZrMe}_2$  in toluene, respectively. The Zr/Cr ratios were 1:1 and 2:1, respectively.

10

The results presented in Table 2 show that the catalyst  $\text{Cp}_2\text{ZrBz}_2$  of Examples 10 to 13 has a highest activity with a Zr/Cr molar ratio of about 0.5:1. When this ratio is increased, the catalyst activity decreases and becomes zero at a ratio of 2:1. The 15 catalyst  $\text{Cp}_2\text{ZrMe}_2$  shows a decreasing activity with increasing ratio Zr/Cr from 0.5:1 to 2:1. Thus, for both catalysts an optimal ratio seems to be Zr/Cr = 0.5:1.

20

25

30

35

TABLE 2

Polymerisation of ethylene in the presence of catalyst  
 Cr/silica + Cp<sub>2</sub>ZrR<sub>2</sub> with various Zr/Cr molar ratios

Ex.	R, R"	Zr/Cr	H <sub>2</sub> (bar)	Temp. (°C)	Activity g/g·h	MFR g/10 min	HLMFR g/10 min
Ex. 10	Bz	0,25	2	93	1115	0.087	16
Ex. 11	Bz	0,5	0,5	94	1656	0.088	13,75
Ex. 12	Bz	1	0,5	93,5	1282	0.034	7,93
Ex. 13	Bz	2	1	95,3	0	-	-
Ex. 14	Me	0,5	0,5	4	1174	0.029	6,02
Ex. 15	Me	1	0,5	94	970	0.014	4,06
Ex. 16	Me	2	0,5	93,6	525	0.021	4,63
Comp. 9	-	-	1	97	617	0,091	14,5

## EXAMPLES 17 TO 22

These examples demonstrate the effect of varying the partial pressure of hydrogen in the reactor when polymerising ethylene in the presence of catalysts  $\text{Cp}_2\text{ZrBz}_2$  and  $\text{Cp}_2\text{ZrMe}_2$ . In 5 all examples the molar ratio Zr/Cr equalled 0.5:1. Polymerisation parameters and obtained results are given in Table 3.

## EXAMPLES 17 TO 20

Polymerisation catalyst: Cr/SiO<sub>2</sub> contacted with  $\text{Cp}_2\text{ZrBz}_2$ .  
10 The catalyst was prepared analogous to example 11 by suspending 1.501 g of reduced 1% by weight of Cr/SiO<sub>2</sub> in 12.473 g of mineral oil in a 50 ml glass bottle provided with a septum. To this mixture was added 0.603 ml of a 10% by weight solution of  $\text{Cp}_2\text{ZrBz}_2$  in toluene and the mixture was stirred for another 1 h. The 15 obtained catalyst was then used in the polymerisation of ethylene according to the general polymerisation procedure outlined above, with hydrogen pressures of 0, 0.5, 1 and 2 bars, respectively.

## EXAMPLES 21 AND 22

20 Example 14 was repeated, except that the hydrogen pressure was 1 bar and 2 bars, respectively.

The results presented in Table 3 show that catalyst  $\text{Cp}_2\text{ZrBz}_2$  and catalyst  $\text{Cp}_2\text{ZrMe}_2$  behave differently in the presence of hydrogen.  
25 Catalyst  $\text{Cp}_2\text{ZrBz}_2$  used in Examples 17 to 21 has a higher activity around 1 bar hydrogen pressure. Increased hydrogen level increases the melt index and lowers the density of the produced polyethylene, which indicates an increasing amount of short chain branching. Catalyst  $\text{Cp}_2\text{ZrMe}_2$  used in Examples 14, 21 and 22 30 responds very little to an increased hydrogen pressure.

TABLE 3

Polymerisation of ethylene in the presence of catalyst  
 Cr/silica + Cp<sub>2</sub>ZrR<sub>2</sub> (Zr/Cr molar ratio 0.5) at increasing H<sub>2</sub> levels

Ex.	R, R''	H <sub>2</sub> (bar)	Temp. (°C)	Activity g/g·h	MFR g/10 min	HLMFR g/10 min	Density g/cm <sup>3</sup>
Ex. 17	Bz	0	92, 8	923	0,06	8,9	0,937
Ex. 18	Bz	0,5	93	1290	0,15	19,8	0,937
Ex. 19	Bz	1	93, 2	1413	0,2	28,2	0,934
Ex. 20	Bz	2	93	1057	1,07	87,6	0,928
Ex. 14	Me	0,5	94	1174	0,029	6,02	0,948
Ex. 21	Me	1	94	1190	0,021	5,89	0,948
Ex. 22	Me	2	94	948	0,034	8,93	0,946
Ex. 9		1	97	617	0,091	14,5	0,949

## EXAMPLE 23

Example 11 was repeated, except that the level of hydrogen was increased to 1 bar.

## 5 EXAMPLE 24

Example 12 was repeated, except that the level of hydrogen was increased to 1 bar.

Polyethylenes produced with catalyst Cr/SiO<sub>2</sub> + Cp<sub>2</sub>ZrBz<sub>2</sub> were  
10 subjected to spectroscopic analysis of end groups with IR and  
13C-NMR. The spectroscopic analysis shows that the branches are mainly ethyl and butyl branches which have been introduced by the copolymerisation of 1-butene and 1-hexene as comonomers produced from ethylene simultaneously with the polymerisation reaction in  
15 the reactor. Obtained results are presented in Table 4.

The results of Table 4 show that there is produced a considerable amount of short chain branching on the polyethylenes during polymerisation. The short chain branching can be controlled by  
20 using catalysts with different Zr/Cr ratios and by adjusting the hydrogen level.

**Table 4**  
**Polymerization of ethylene in the presence of catalyst Cr/SiO<sub>2</sub> + Cp<sub>2</sub>ZrBz<sub>2</sub>**

Ex.	Zr/Cr mol/mol	H <sub>2</sub> (bar)	Temp. (°C)	MI g/10 min	Density g/10 min	Methyl <sup>1)</sup> pr. 1000 °C	Vinyl <sup>1)</sup> pr. 1000 °C	Trans <sup>1,2)</sup> pr. 1000 °C	Ethyl <sup>1,3)</sup> pr. 1000 °C	Butyl <sup>1,3)</sup> pr. 1000 °C
Ex. 11	0,5	0,5	94	0,09	0,945	4,2	0,89	0,016	2,0	1,7
Ex. 23	0,5	1	97	0,82	0,935	8,3	0,91	0,021	4,0	4,6
Ex. 12	1	0,5	93,5	0,03	0,94	3,7	0,81	0,02	2,4	1,8
Ex. 24	1	1	97	0,35	0,945	5,5	0,95	0,028	1,8	2,0
Comp. 9		1	97	0,09	0,949	1,3	0,87	0,002	0,3	0,3

1) From IR measurements

2) Transvinylene fragments

3) From <sup>13</sup>C-NMR measurements

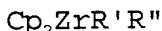
C L A I M S

5 1. A catalyst system for the polymerisation of ethylene, comprising chromium oxide and a metallocene supported on an inorganic support, **characterised** by:

- a) said support being a particulate inorganic oxide;
- b) the chromium of said chromium oxide being in a reduced oxidation state,

10 and

- c) a metallocene compound having the formula:



wherein each Cp, being equal or different, is an unsubstituted 15 or substituted cyclopentadienyl compound, and R' and R'', independant of each other, are selected from the group comprising alkyls having 1 to 6 carbon atoms, unsubstituted or substituted benzyl, and phenoxy substituted with alkyls having 1 to 6 carbon atoms, and R' or R'' may be a halide.

20 2. A catalyst system according to claim 1, **characterised** in that the cyclopentadienyl compound is substituted with radicals selected from the group comprising unsubstituted and substituted linear, branched, cyclic or partially cyclic alkyl 25 radicals and annelated cyclic radicals, containing 1 to 20 carbon atoms; unsubstituted and substituted monocyclic or polycyclic aryl radicals which optionally also may contain hetero atoms; and aralkyl radicals; the substituents on the cyclopentadienyl ring may also form annelated structures 30 comprising one or more fused benzene, naphthalene or cyclohexene rings, which optionally may contain hetero atoms, and the two cyclopentadienyl rings may also be connected through a bridge.

35 3. A catalyst system according to claim 1, **characterised** in that R' and R'' are selected from the group comprising chloride, methyl, benzyl or phenoxyethyl, and combinations thereof.

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## ART 34 AMDT

4. A catalyst system according to claims 1 to 3, **characterised** in that Cp is an unsubstituted cyclopentadienyl and that R' and R" are equal and are either methyl or benzyl.
5. 5. A catalyst system according to claims 1 to 4, **characterised** in that the metallocene is bis-cyclopentadienyl-zirconium dibenzyl.
10. 6. A catalyst system according to claim 1, **characterised** in that said support is a particulate, inorganic oxide selected from the group comprising alumina, silica, titania, zirconia, magnesia, and combinations thereof.
15. 7. A catalyst system according to claim 6, **characterised** in that said support is silica having the shape of spherical or spheroidal particles with a particle size in the range of from 20 µm to 150 µm, and a surface area from 200 m<sup>2</sup>/g to 600 m<sup>2</sup>/g.
20. 8. A catalyst system according to claim 1, **characterised** in that the chromium is present in an amount from 0.1 % to 10 % by weight calculated as metallic chromium based on the weight of the chromium/silica catalyst of a) and b).
25. 9. A catalyst system according to claim 8, **characterised** in that the chromium is present in an amount from 0.5 to 2,0 % by weight of chromium.
30. 10. A catalyst system according to claim 1 to 5, **characterised** by a molar ratio between zirconium and chromium in the final catalyst in the range from 0.1:1 to not higher than 2:1.
35. 11. A catalyst system according to claim 9, **characterised** in that said molar ratio between zirconium and chromium is from 0.5:1 to 1:1.
12. A method for the preparation of the catalyst system of claim 1, comprising the steps of:

a) calcining a support being a particulate, inorganic oxide selected from the group comprising alumina, silica, titania, zirconia, magnesia, and combinations thereof,

5 b) joining onto the surface of said support a chromium- organic compound to obtain a catalyst precursor,

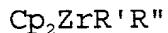
c) subjecting said catalyst precursor to oxidising conditions to obtain the chromium in an oxidised state,

d) subjecting said catalyst precursor to reducing conditions to obtain a prereduced catalyst,

10 **characterised by**

e) reducing the oxidised chromium to obtain the main part thereof in a bivalent oxidation state

f) contacting said reduced catalyst with a metallocene compound having the formula:



15 wherein each Cp, equal or different, is an unsubstituted or substituted cyclopentadienyl compound, and R' and R'', independant of each other, are selected from the group comprising alkyls having 1 to 6 carbon atoms, unsubstituted or 20 substituted benzyl, and phenoxy substituted with alkyls having 1 to 6 carbon atoms, and R' or R'' may be a halide.

No. EL 702626043US

<b>DECLARATION AND POWER OF ATTORNEY FOR UTILITY OR DESIGN</b>		Attorney Docket No.	FRD-043
		First Named Inventor	Follestad
<b>COMPLETE IF KNOWN</b>			
		Application Serial Number	09/673,121
		Filing Date	October 10, 2000
		Group Art Unit	Not Yet Assigned
		Examiner Name	Not Yet Assigned
<input type="checkbox"/> Declaration <input checked="" type="checkbox"/> Declaration Submitted with      Submitted after Initial Initial Filing      Filing (surcharge 37 CFR 1.16(e) required)			

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

CATALYST SYSTEM FOR ETHYLENE POLYMERISATIONS

(Title of the Invention)

the specification of which

is attached hereto  
OR

was filed on  
(MM/DD/YYYY)

10/10/2000

as United States Application Serial Number or PCT International

Application Number 09/673,121 and was amended on (MM/DD/YYYY) 10/10/2000 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose to the Patent Office all information known by me to be material to patentability as defined in 37 CFR 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	Certified Copy Attached? NO
981631	Norway	04/08/1998	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	<input checked="" type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>

Additional foreign application numbers are listed on a supplemental priority data sheet attached hereto.

I hereby claim the benefit under 35 U.S.C. 119(e) of any United States provisional application(s) listed below.

Application Serial Number(s)	Filing Date (MM/DD/YYYY)	<input type="checkbox"/> Additional provisional application serial numbers are listed on a supplemental priority data sheet attached hereto.

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Declaration and Power of Attorney for Utility or Design Patent Application  
 Serial No. 09/673,121  
 Atty. Docket No. FRD-043  
 Page 2 of 3

## DECLARATION - Utility or Design Patent Application

I hereby claim the benefit under 35 U.S.C. 120 of any United States application(s), or 365(c), of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of 35 U.S.C. 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application or PCT Parent Serial Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
PCT/NO99/00116	04/07/1999	

Additional U.S. or PCT International application numbers are listed on a supplemental priority data sheet attached hereto.

As a named inventor, I hereby appoint the following registered practitioners to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:  Customer Number →  Place Customer Number Bar Code Label Here

OR

Registered practitioner(s) name/registration number listed below

Name	Registration Number	Name	Registration Number
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John V. Bianco	36,748	Joseph B. Milstein	42,897
Isabelle A.S. Blundell	43,321	David G. Miranda	42,898
Maurice A. Bresnahan	44,559	Ronda P. Moore	44,244
Michael H. Brodowski	41,640	Indranil Mukerji	P-46,944
Jennifer A. Camacho	43,526	Edmund R. Pitcher	27,829
Joseph A. Capraro, Jr.	36,171	Michael A. Rodriguez	41,274
John J. Cetter	38,116	Jamie H. Rose	45,054
John V. Foscier	42,545	R. Stephen Rosenholm	45,283
Steven J. Frank	33,997	Christopher W. Stamos	35,370
Brian M. Gaff	44,691	Diana M. Steel	43,153
Michael J. Giannetta	42,374	Joseph P. Sullivan	45,349
Duncan A. Greenhalgh	38,678	Robert J. Tosti	35,393
William G. Guerin	41,047	Thomas A. Turano	35,722
Jonathan A. Harris	44,744	Michael J. Twomey	38,349
Ira V. Hoffman	41,039	Christine C. Vila	39,061
Danielle L. Herritt	43,670	Patrick R.H. Waller	41,418
Douglas J. Kline	35,574	Daniel A. Wilson	45,508
John D. Lanza	40,060	Yin P. Zhang	44,372
Kurt W. Lockwood	40,704		

Additional registered practitioners named on supplemental Registered Practitioner Information sheet attached hereto.

Direct all correspondence to:

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 High Street Tower  
 125 High Street  
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 Tel. No.: (617) 248-7000  
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## Declaration and Power of Attorney for Utility or Design Patent Application

Serial No. 09/673,121

Art. Docket No. FRD-043

Page 3 of 3

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor:		<input type="checkbox"/> A petition has been filed for this unsigned inventor							
Given Name (first and middle (if any))		Family Name or Surname							
Ariild		Folkestad							
Inventor's Signature	<i>Ariild Folkestad</i>						Date	14.11.00	
Residence	City	Stathelle	State		Country	Norway	<input checked="" type="checkbox"/>	Citizenship	Norwegian
Post Office Address	Damstien 10								
P.O. Address (line 2)	City	Stathelle	State		ZIP	N-3960	Country	Norway	
<input checked="" type="checkbox"/> Additional inventors are being named on the supplemental Additional Inventor(s) sheet(s) attached hereto.									
Name of Additional Joint Inventor, if any:	<input type="checkbox"/> A petition has been filed for this unsigned inventor								
Given Name (first and middle (if any))		Family Name or Surname							
Klaus-Joachim		Jens							
Inventor's Signature	<i>Klaus-Joachim</i>						Date	14.11.00	
Residence	City	Langesund	State	<input checked="" type="checkbox"/>	Country	Norway	<input type="checkbox"/>	Citizenship	German
Post Office Address	Kjærlighetsstien 19								
P.O. Address (line 2)	City	Langesund	State		ZIP	N-3970	Country	Norway	
Name of Additional Joint Inventor, if any:	<input type="checkbox"/> A petition has been filed for this unsigned inventor								
Given Name (first and middle (if any))		Family Name or Surname							
Richard		Blom							
Inventor's Signature							Date		
Residence	City	Oslo	State		Country	Norway	<input type="checkbox"/>	Citizenship	Norwegian
Post Office Address	Sørbyhaugen 38								
P.O. Address (line 2)	City	Oslo	State		ZIP	N-0377	Country	Norway	

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14/11 '00 17:07 FAX 020 7208 0700

FRANK B. DEHN

11/09/00 THU 14:18 FAX

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Supplemental Sheet of Declaration and Power of Attorney for Utility or Design Patent Application  
Serial No. 09/673,121  
Amy Docket No. FRD-043

DECLARATION AND  
POWER OF ATTORNEY FOR UTILITY  
OR DESIGN PATENT APPLICATION

ADDITIONAL INVENTOR(S)  
Supplemental Sheet  
Page 1 of 1

Name of Additional Joint Inventor, if any:	<input type="checkbox"/> A petition has been filed for this unsigned inventor							
Given Name (first and middle [if any])	Family Name or Surname							
Ivar Martin	Dahl							
Inventor's Signature					Date			
Residence	City	Oslo	State		Country	Norway	Citizenship	Norwegian
Post Office Address	Kongsberggt. 6							
P.O. Address (line 2)	City	Oslo	State		ZIP	N-0468	Country	Norway
Name of Additional Joint Inventor, if any:	<input type="checkbox"/> A petition has been filed for this unsigned inventor							
Given Name (first and middle [if any])	Family Name or Surname							
Inventor's Signature					Date			
Residence	City		State		Country		Citizenship	
Post Office Address								
P.O. Address (line 2)	City		State		ZIP		Country	

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11/08/00 THU 14:19 FAX

FRANK B. DEHN

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003-008

No. EL 702 626 043 US

003

<b>DECLARATION AND POWER OF ATTORNEY FOR UTILITY OR DESIGN</b>		Attorney Docket No.	FRD-043
		First Named Inventor	Follestad
<b>COMPLETE IF KNOWN</b>			
		Application Serial Number	09/673,121
		Filing Date	October 10, 2000
		Group Art Unit	Not Yet Assigned
		Examiner Name	Not Yet Assigned

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**CATALYST SYSTEM FOR ETHYLENE POLYMERISATIONS**

(Title of the Invention)

the specification of which

 is attached hereto

OR

 was filed on  as United States Application Serial Number or PCT International (MM/DD/YYYY)Application Number  and was amended on (MM/DD/YYYY)  (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose to the Patent Office all information known by me to be material to patentability as defined in 37 CFR 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES <input type="checkbox"/> NO <input type="checkbox"/>
981631	Norway	04/08/1998	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>

 Additional foreign application numbers are listed on a supplemental priority data sheet attached hereto.

I hereby claim the benefit under 35 U.S.C. 119(e) of any United States provisional application(s) listed below.

Application Serial Number(s)	Filing Date (MM/DD/YYYY)	<input type="checkbox"/> Additional provisional application serial numbers are listed on a supplemental priority data sheet attached hereto.

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## Declaration and Power of Attorney for Utility or Design Patent Application

Serial No. 09/673,121

Atty. Docket No. FRD-043

Page 2 of 3

**DECLARATION – Utility or Design Patent Application**

I hereby claim the benefit under 35 U.S.C. 120 of any United States application(s), or 365(c), of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application or PCT Parent Serial Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
PCT/NO99/00116	04/07/1999	

Additional U.S. or PCT international application numbers are listed on a supplemental priority data sheet attached hereto.

As a named inventor, I hereby appoint the following registered practitioners to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:  Customer Number →  Registered practitioner(s) name/registration number listed below

Name	Registration Number	Name	Registration Number
Steven M. Bauer	31,481	Thomas C. Meyers	36,989
John V. Bianco	36,748	Joseph B. Milstein	42,897
Isabelle A.S. Blundell	43,321	David G. Miranda	42,898
Maureen A. Bresnahan	44,559	Ronda P. Moore	44,244
Michael H. Brodowski	41,640	Indranil Mukerji	P-46,944
Jennifer A. Camacho	43,526	Edmund R. Pitcher	27,829
Joseph A. Capraro, Jr.	36,471	Michael A. Rodriguez	41,274
John J. Cotter	38,116	Jamie H. Rose	45,054
John V. Forcier	42,545	R. Stephen Rosenholm	45,283
Steven J. Frank	33,497	Christopher W. Stamos	35,370
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Michael J. Giannetta	42,574	Joseph P. Sullivan	45,349
Duncan A. Greenhalgh	38,678	Robert J. Tosti	35,393
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## Declaration and Power of Attorney for Utility or Design Patent Application

Serial No. 09/673,121  
 Atty. Docket No. FRD-043  
 Page 3 of 3

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Name of Sole or First Inventor:		<input type="checkbox"/> A petition has been filed for this unsigned inventor						
Given Name (first and middle [if any])		Family Name or Surname						
Arild		Follestad						
Inventor's Signature							Date	
Residence	City	Stathelle	State		Country	Norway	Citizenship	Norwegian
Post Office Address	Damstien 10							
P.O. Address (line 2)	City	Stathelle	State		ZIP	N-3960	Country	Norway
<input checked="" type="checkbox"/> Additional inventors are being named on the supplemental Additional Inventor(s) sheet(s) attached hereto.								
Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor						
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Klaus-Joachim		Jens						
Inventor's Signature							Date	
Residence	City	Langesund	State		Country	Norway	Citizenship	German
Post Office Address	Kjærlighetsstien 19							
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Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor						
Given Name (first and middle [if any])		Family Name or Surname						
<i>Richard</i>							<i>Blom</i>	
Inventor's Signature	<i>X Richard Blom</i>						Date	<i>X 15 Nov 2000</i>
Residence	City	Oslo	State	NOX	Country	Norway	Citizenship	Norwegian
Post Office Address	Sørbyhaugen 30							
P.O. Address (line 2)	City	Oslo	State		ZIP	N-0377	Country	Norway

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Supplemental Sheet of Declaration and Power of Attorney for Utility or Design Patent Application  
 Serial No. 09/673,121  
 Atty. Docket No. FRD-043

<b>DECLARATION AND POWER OF ATTORNEY FOR UTILITY OR DESIGN PATENT APPLICATION</b>	<b>ADDITIONAL INVENTOR(S)</b> <b>Supplemental Sheet</b> <b>Page 1 of 1</b>
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Name of Additional Joint Inventor, if any:	<input type="checkbox"/> A petition has been filed for this unsigned inventor							
Given Name (first and middle [if any])	Family Name or Surname							
Ivar Martin	Dahl							
Inventor's Signature	<i>Ivar M Dahl</i>			Date	15. nov. 2000			
Residence	City	Oslo	State	N 0	Country	Norway	Citizenship	Norwegian
Post Office Address	Kongsberggt. 6							
P.O. Address (line 2)	City	Oslo	State		ZIP	N-0468	Country	Norway
Name of Additional Joint Inventor, if any:	<input type="checkbox"/> A petition has been filed for this unsigned inventor							
Given Name (first and middle [if any])	Family Name or Surname							
Inventor's Signature							Date	
Residence	City		State		Country		Citizenship	
Post Office Address								
P.O. Address (line 2)	City		State		ZIP		Country	

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